ANALYTICAL METHOD

TITLE: Nitrogen, Ammonia – Automated Analysis

DEPARTMENT: Inorganic – Wet Chemistry

APPLICATION: Drinking, Surface and ground waters and Solid matricies

REFERENCE: EPA 600 4-79-020, Revised March 1983, Method 350.1

PROCEDURE SUMMARY:

This method is performed following distillation of the samples and is based on the Berthelot reaction. Ammonia reacts with alkaline phenol, then with sodium hypochlorite to form indophenol blue. Sodium nitroprusside (nitroferricyanide) is added to enhance sensitivity. The absorbance of the reaction product is measured at 630 nm, and is directly proportional to the original ammonia concentration in the sample.

REPORTING LIMITS: Water: 0.10 mg/L; Soil: 5 mg/kg.

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Annual Review

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SAMPLE HANDLING AND PRESERVATION:

Preserve samples with concentrated sulfuric acid, 2 mL per liter, and store at 4 °C. The maximum sample holding time prior to analysis is 28 days. ALL samples are distilled prior to analysis. For Distillation, see EN CHEM SOP WCM-25.

SAFETY:

The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Laboratory staff should observe all safety procedures as outlined in the Laboratory Health and Safety Manual. Staff should consult Materials Safety Data Sheets (MSDS) for information on specific chemicals.

INTERFERENCES:

Calcium and magnesium ions may precipitate if present in sufficient concentration. Tartrate or EDTA is added to the sample in-line in order to prevent this problem. Color, turbidity and certain organic species may interfere. Turbidity is removed by manual filtration. Sample color may be corrected for by running the samples through the manifold without color formation.

APPARATUS AND MATERIALS:

LACHAT Quikchem Automated Ion Analyzer
630 nm interference filter
75 cm sample loop
10-107-06-1-B ammonia manifold
Volumetric flasks: 100 mL, 1000 mL
Pipettor: adjustable, fixed

REAGENTS AND STANDARDS:

NOTE: All solutions must be made with ammonia free water.

Prepare Sodium Phenolate

Caution: Wear gloves. Phenol causes severe burns and is rapidly absorbed into the body through the skin.

Dissolve 88 mL of 88% liquefied phenol or 83 g crystalline phenol (C_6H_5OH) in approximately 600 mL of DI water. While stirring, slowly add 32 g sodium hydroxide (NaOH). Cool, dilute to 1 L and invert to mix. Shelf life is 1 year.

Prepare Sodium Hypochlorite:

In a 500 mL volumetric flask dilute 250 mL regular Clorox bleach to mark with Milli-Q water. Shelf life is 1 year.

Prepare Buffer solution:

Dissolve 50.0 g disodium ethylenediamine tetraacetate dihydrate [$Na_2EDTA\text{-}2H_2O$] and 9.0 g sodium hydroxide (NaOH) in approximately 900 mL Milli-Q water. Dilute to 1 L with Milli-Q water. Shelf life is 1 year.

Prepare Sodium Nitroprusside:

Dissolve 3.50 g of sodium nitroprusside (sodium nitroferricyanide [$Na_2Fe(CN)_5NO\bullet 2H_20$]) in approximately 900 mL of Milli-Q water. Dilute to 1 L with Milli-Q water. Shelf life is 1 year.

Prepare Carrier and Diluent (0.20% Sulfuric Acid):

Add 2.0 mL concentrated sulfuric acid (H_2SO_4) to 900 mL of Milli-Q water. Dilute to 1 L with Milli-Q water. Shelf life is 1 year.

Prepare Ammonium Chloride stock solution, NH_4Cl, 1.0 mL = 1.0 mg NH_3-N (1000 ppm):

Dissolve 3.819 grams NH_4Cl in approximately 900 mL of Milli-Q water. Dilute to 1 L with Milli-Q water. Shelf life is 1 year.

Prepare Ammonium chloride working solution, 1 mL = 0.10 mg NH_3-N (100 ppm):

Dilute 10 mL of stock solution to 100 mL in a volumetric flask with Milli-Q water. Prepare weekly.

Prepare Ammonium chloride calibration standards:

Dilute 5.0, 3.75, 2.5, 1.25, 0.50, 0.10 mL of working solution to 100 mL in a volumetric flask with Diluent to make 5.0, 3.75, 2.5, 1.25, 0.50, 0.10 ppm standards, respectively. Prepare 0.50, 0.10 ppm daily. Prepare 5.0, 3.75, 2.5, 1.25 ppm standards weekly.

Prepare Ammonium chloride check standard:

Dilute 2.0 mL of 2nd source working solution to 100 mL in a volumetric flask with Diluent to make a 2.0 ppm standard. Prepare daily.

PROCEDURE:

1. Allow 15 min for heating unit to warm to 60° C.

2. Connect 10-107-06-1-B manifold.

3. Install 630 nm interference filter.

4. Install 75 cm sample loop.

CALIBRATION:

Instrument calibration is performed using the prepared standards at the following concentrations (mg/L): 0.10, 0.50, 1.25, 2.5, 3.75 and 5.0. Analyze the standards beginning with the highest and

working to the lowest standard. The correlation coefficient for the curve must be 0.995 or greater. The calibration must be verified as specified in Quality Control, below.

NOTE: All analyses on the LACHAT are performed using one replicate.

SYSTEM NOTES:

If baseline drifts, peaks are too wide, or other problems with precision arise, clean the manifold by the following procedure.

1. Place all reagent lines in deionized water and pump to clear reagents
2. Place all reagent lines in 1 M hydrochloric acid (1:12 concentrated HCL), pump for several minutes.
3. Place all reagent lines in deionized water and pump until the HCL is thoroughly washed out.
4. Resume pumping reagents.

QUALITY CONTROL:

- Correlation Coefficient (r value)
  The correlation coefficient, the measure of linearity of the standard curve, must be 0.995 or greater.
- Initial Calibration Verification (ICV)
  The ICV must be run immediately after calibration and meet 90-110% control limits. If not, recalibrate.
- Initial Calibration Blank (ICB)
  The ICB must be analyzed after the ICV and be less than the absolute value of the estimated quantitation limit (EQL). If not, recalibrate.
- Laboratory Control Sample (LCS) Distilled Standard
  The LCS is carried through all prep procedures and analyzed with a frequency of 5%. Recovery must meet the current control limit** of 72-116%.
- Method Blank
  The MB is carried through all prep procedures and analyzed with a frequency of 5%. Rejection criteria is < LOD. Other criteria may apply, such as regulatory limit and analyte concentration in samples.
- Continuing Calibration Verification (CCV)
  The CCV is analyzed after every 10 analytical samples and meet 90-110% control limits. If it is not within control, stop analysis, and recalibrate. All samples analyzed since the last successful CCV must be reanalyzed.

. Continuing Calibration Blank (CCB)
The CCB is analyzed after every CCV and be less than the absolute value of the EQL. If it is not within control, stop analysis, and recalibrate. All samples analyzed since the last successful CCB must be reanalyzed.

. Matrix Spike
A spike must be performed on each group of samples of a similar matrix type with a frequency of 5%. Recovery must meet the current control limit** of 80-114%.

. Matrix Spike Duplicate
A matrix spike duplicate must be analyzed on each group of samples of a similar matrix type with a frequency of 5%. Recovery must meet the current control limits for accuracy and the difference between the MS and MSD must meet current control limits for precision. The current control limit** is 0-14% RPD.

** Control limits are updated periodically. The control limits that are in use at the time of analysis will be used and made available to data validators.

CALCULATIONS:

Samples:

The instrument provides calculated sample results in mg/L, calculations are only necessary if a dilution was used.

Raw Data Value (mg/L) x Dilution Factor = Total Ammonia (mg/L)

Accuracy:

A matrix spike and matrix spike duplicate must be performed on each group of samples of a similar matrix type with a frequency of 5% and meet the current control limits for accuracy.

Spike calculation:

$$\% \text{ Recovery} = \frac{SSR-SR}{SA}$$

SSR = Spiked Sample Result
SR = Sample Result
SA = Spike Added

If there is insufficient volume available for an MS/MSD, perform an LCS/LCSDUP.

Precision:

A matrix spike duplicate must be analyzed on each group of samples of a similar matrix type with a frequency of 5% and meet the current control limits for precision.

Relative percent difference (RPD) calculation:

$$RPD = \frac{|MS-MSD|}{(MS+MSD)/2} \times 100$$

MS = Matrix Spike Value
MSD = Matrix Spike Duplicate Value

If there is insufficient volume available for an MS/MSD, perform an LCS/LCSDUP.

POLLUTION PREVENTION and WASTE MANAGEMENT:

Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Laboratory staff should order and prepare only those quantities of reagents that will be used prior to the expiration date. Other appropriate measures to minimize waste generation should be brought to the attention of laboratory management. All laboratory waste shall be handled as directed by the Laboratory Waste Management Plan and Hazardous Waste Contingency Plan.